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Investigating the Synergistic Effect of Bauxsol™ in an Epoxy Intumescent Coating System.

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Abstract

Bauxsol™ (BX) is a refined alumino-silicate waste derived from the brine neutralization of bauxite residue (BR). Due to this brine treatment, Bauxsol™ contains hydrotalcite-like minerals in addition to the zeolitic minerals, metal oxides and hydroxides found in bauxite residue. In this work, investigations are carried out to determine the effect of Bauxsol™ addition on the fire performance of an Ammonium Polyphosphate-based epoxy intumescent coating system. Surface imaging, thermal analysis, elemental and phase analyses of the material were carried out using Field Emission Scanning Microscope, Thermogravimetric Analysis, X-ray Florescence Spectroscope and X-ray Diffraction respectively. Fire performance of the system was evaluated with Bunsen burner test for heat shielding capacity. The fire behavior was subsequently analyzed using the generated heat curves and thermogravimetric curves of the systems.

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Keywords: Bauxsol™; hydrotalcite ; synergistic filler; intumescent coating

1. Introduction

Bauxsol™ (BX), sometimes referred to as Bayer hydrotalcite is the trade name of brine neutralized bauxite residue (BR). It is one of the few established products in the 'waste to feedstock' quest for BR utilization [1-3]. Bauxsol is produced by treating the caustic slurry from the Bayer process in sea water leading to the conversion of soluble hydroxides and carbonates into less soluble layered hydroxides, carbonates and hydroxyl-carbonates of the base metals, and giving a less caustic liquor which can then be safely disposed or utilized. Thus, in addition to the aluminium silicates, metal oxides and hydroxides found in red mud, Bauxsol™ incorporates small amount of layered double hydroxides (LDH), aragonites and calcite [4-6]. LDH are brucite-like structured anionic clays having the general formula $[M^{2+}_{1-x}M^{3+}_{x}9(OH)_2]^{x+}A^{m-}_{x/m}\cdot nH_2O$. In the bauxite residue, LDH occur as hydrocalumite (HC) and hydrotalcite (HT) due to the replacement of a trivalent Al^{3+} from gibbsite with divalent Mg^{2+} or Ca^{2+} from the brine. To balance the net positive charge, carbonate ions are adsorbed in the interlayer. Also resident in the interlayer are free and adsorbed water molecules [5, 6] .

LDHs have been reported in the literatures as fire retardant fillers for polymer. Earlier works have compared hydrotalcite-like layered hydroxide to the popular metal hydroxides fire retardants, aluminum hydroxides and magnesium hydroxides and, reported lowest heat release rate, highest ignition time and highest residual mass with HT [7-9]. The synergistic effect of hydrotalcite in phosphorus-based fire retardant ethylene vinyl acetylene (EVA) has also been reported. The intercalation of

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phosphorus in the interlayer was observed to improve char forming ability of the host matrix [9]. Recent publications have confirmed continuous interest in the fire retarding ability of HTs [10-12]. The fire retarding ability of HTs has been credited to the endothermic decomposition of the interlayer water molecules and carbonates, and to the barrier effect of the layered sheets. Though BX has been widely studied for its adsorptive property and has been adapted to an array of adsorptive applications, the need remains to diversify its usage and thereby create more avenues for the safe disposal of BR. In this work therefore, its suitability as filler in intumescent coating system was investigated.

Intumescent coatings (IC) are passive, fire retardant paints which decompose at high temperature into multicellular, porous char with insulative ability to protect the substrate material from heat. In recent years, intumescent coatings have become quite popular in the fire protection of steel structures and other facilities. In the events of fire, the intumescent char effectively provides a heat shielding front for the steel substrate, extending the time before failure and creating more time for evacuation of life and combative firefighting [13-17].

2. Experimentation

2.1. Materials

Bauxsol (BX) was obtained from Virotec, Australia. It had a BET surface area of 26.82 m^2/g and a pore size of 10.75 nm. Ammonium polyphosphate was purchased from Clariant (Malaysia) Sdn Bhd. The binder, Bisphenol A epoxy resin BE-188 (BPA) and ACR Hardener H-2310 polyamide amine were purchased from Mc Growth Chemical Sdn Bhd. Malaysia. Expandable graphite (EG), melamine (MEL) and boric acid (BA) were supplied by Sigma-Aldrich, Sdn Bhd, Malaysia. Table-1 shows the oxide composition of the BX used in this study as analyzed by a Bruker X-ray Florescence Spectrometer.

Table 1. Oxide Composition of Sea-water neutralized red mud (Bauxsol)

Component	Fe_2O_3	Al_2O_3	SiO_2	TiO_2	CaO	Na_2O	Cl	P_2O_5	ZrO_2	MgO
Mass (wt%)	48.9	13.3	12.4	9.45	8.80	2.16	1.81	1.02	0.588	0.531

2.2. Sample preparation and characterization

The BX was dried in a Carbolite 450 Oven at 105°C for 24 hours to remove physically bonded water and prevent clogging of sieve during particle size analysis. This was ground lightly in a mortar and passed through a set of sieves to obtain an even particle size distribution. ± 63 μm sized BX was used for the coating. The microscopic structure of the mud was studied using a Field emission scanning electron spectrometer. Phase analysis was carried out on a Bruker type X-ray Diffractometer. Its thermal properties were analyzed from 30°C to 1000°C in Nitrogen on an Exstar TG/DTA 6300, S11 Model at the SIRIM Bhd. Sdn.

2.3. Preparation of intumescent coatings

Several Bauxsol intumescent coatings (BX-IC) were prepared in an epoxy matrix by varying the mass of BX in the base formulation. The base formulation was made up of ammonium polyphosphate-melamine-boric acid-expandable graphite (APP-MEL-BA-EG) in the ratio 2:1:2:1 [15]. Coatings were applied on 100 x 100 x 3 mm steel plates for Bunsen burner test. Filler percent loadings of 0-5% were used and the coatings were referred to as BX-IC0 to BX-IC5 respectively.

2.4. Performance Characterization

Heat shielding capacity was determined using the Bunsen burner test. The heat curve was maintained at 700 $\pm$ 300 °C following closely the ASTM E 119 Standard Fire Curve for building structures. An impacting flame from a butane gas was applied to 100 x 100 x 3 mm coated steel plates for 60 minutes. Three K-type thermocouples were attached to the uncoated face, one directly at the point of impacting flame and the remaining two, equidistant from it across the diagonal. Readings were recorded using an Anritsu AM-800K data logger. Average steel back temperature was plotted against time.

The residual mass and thermal behaviour of each formulation were determined on a Perkin Elmer Pyris Thermogravimetric Analyser. Pyrolysis of the samples were achieved at a heating rate of 10°C/min from 30°C to 800°C inert environment using nitrogen as purging gas.

3. Results and Discussions

3.1. Fire Retarding Properties of Bauxsol

The micro image of the residue shown in Figure-1 revealed a heterogeneous array of mineral structures, mostly platy layered hydroxides overlying finer, needle-like structures suspected to be zeolitic sodalities and other spheroidal nano particles. The high content of nano plates implies a significant barrier effect could be expected by the incorporation of the sea-water neutralized bauxite residue into existing intumescent coating formulations. The phase analysis in Figure 2 revealed hydrates of aluminium as gibbsite (JCPDS 70 2038) and boehmite (JCSPD 49 0133). The peaks at 2θ, 11.8 and 61.4 are usually assigned to HT [18, 19]. In sea water neutralized BR, the peak at 2θ, 12 was detected as a weak peak overshadowed by the more intense boehmite peak [20]. This same phenomenon is suspected here as boehmite peaks are found at 2θ, 14 and 2θ, 64 so close to the supposed HT peaks. The presence of these hydrates and the calcite (JCPDS 83 0578) will expectedly act in the gas phase by the endothermic release of gaseous water and carbon dioxide to augment the intumescent and diluent effects of ammonium released by the decomposition of ammonium polyphosphate (APP) and melamine (MEL). The additional presence of periclase (JCSPD 75 1525), a refractory metal oxide will lead to higher residual mass and a more efficient insulative shield.

Thermogravimetric result in Figure 3 showed Bauxsol to be a thermally stable material with a mass loss of 16 % at 1000 °C. Mass loss was observed as early as 50 °C due to loss of surface and interlayer water by the layered hydroxides (LDH). The highest mass loss rates of 110 µg/min and 60 µg/min from the DTG graph of Figure 4 were observed around 300 °C due to dehydroxylation of the LDH and from 650-750 °C due to decarbonation of calcite respectively. Dehydroxylation of boehmite and probably decarbonation of the HT also occurred around 400-450 °C judging by the small peak in that region. The mass loss of 16 % as a stand-alone action may not impact much endothermic effect on the fire retardant capacity of the APP/EG system, but the coincidental occurrence of dehydroxylation with commencement of the melt phase may have a positive effect on melt rheology and consequently on char structure and insulative capacity. Similar effect was observed in our previous study with BR [21]. Nevertheless, the surface migration of the platy mineral content and consequent high residual mass will create an effective physical barrier against heat and mass loss.

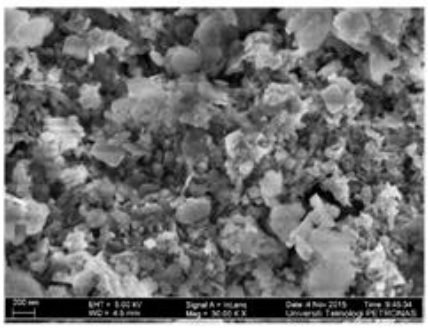

Fig. 1. SEM image of Bauxsol

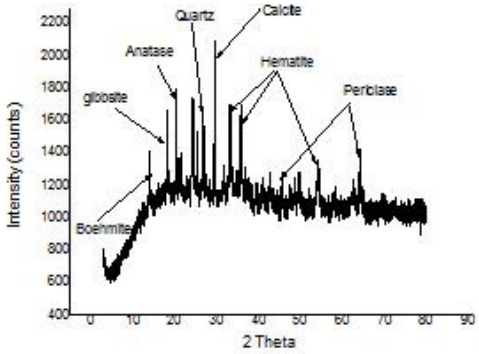

Fig. 2. Xray Diffractogram of Bauxsol

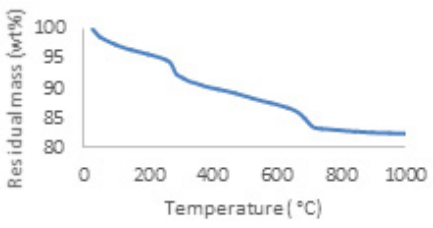

Fig. 3. TGA curve of Bauxsol

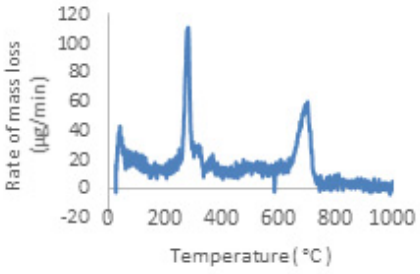

Fig. 4. DTG curve of Bauxsol

3.2. Heat shielding effects of Bauxsol

Results of Fire test in figures 5 and 6 showed the BX-filled ICs to have better resistant to thermal oxidation compared to the unfilled system, BX-IC0. They also revealed an increasing resistance to flame spread and thermal oxidation with filler addition. The improved resistance to flame spread is due to the additional endothermic effect provided by the diluent H_2O and CO_2 released by Bauxsol™ degradation. From the heat curve of Figure 5, it can be observed that BX-IC1 followed by BX-IC2 have the lowest initial temperature rise. This was due to the early dehydroxylation experienced by these systems around 300°C as reflected in the thermogravimetric curves of Figure 7.

Thus, despite the higher residual mass of BX-IC0 at 39%, BX-IC1 is seen to have better oxidative resistance due to the combined influence of dehydroxylation which provided additional heat sinking effect plus the thermal and mass barrier provided by the alumino-silicates and layered hydroxides. However as combustion was sustained, faster temperature rise and greater flame spread were experienced by BX-IC1 and BX-IC2 due to lower residual masses compared to the other BX-filled systems.

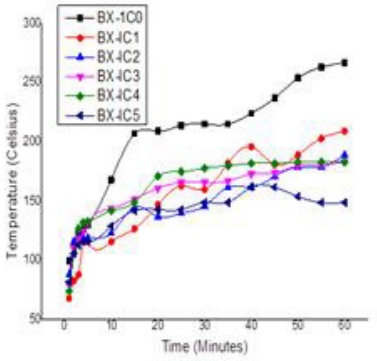

Fig.5. Temperature-time curve of Bauxsol filled Ammonium polyphosphate-based intumescent coating

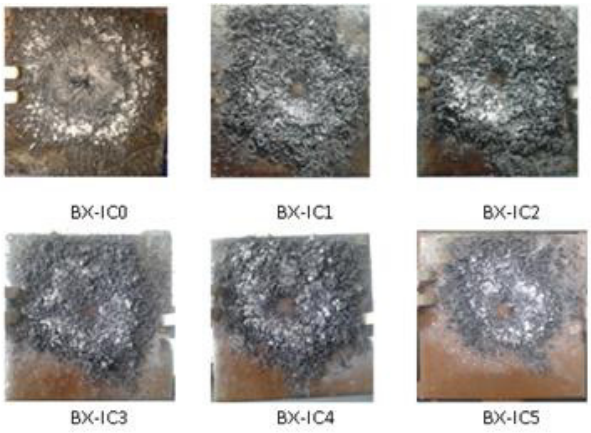

Fig. 6. Bauxsol-filled Intumescent paint coated steel plates after 60 mins of hydrocarbon jet firing

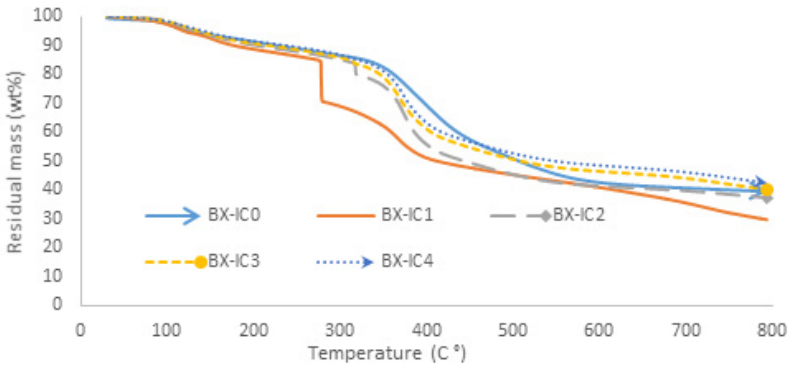

Fig. 7. Thermogravimetric curves of Bauxsol-filled Intumescent Paints

BX-IC1 had the highest steel back temperature of 209 °C among the BX-filled systems, slight improvement was recorded at 2% loading with a steel back temperature of 189 °C. BX-IC3 and BX-IC4 had similar insulative capacity at 183°C. The lowest temperature was recorded at 5% loading with a steel back temperature of 149 °C while the unfilled, BX-IC0 had the highest steel back temperature of 267 °C after 60 minutes of hydrocarbon firing with butane gas.

4. Conclusion

In this work, the effect of Bauxsol as a filler in an ammonium-expandable graphite intumescent system has been investigated and found to be synergistic. Heat shielding performances of the filled and the unfilled systems were compared using the Bunsen burner test. The filled systems were found to perform better than the unfilled due to additional endothermic effect provided by the hydrated minerals, improved barrier effect provided by the layered hydroxides platy silicates and increased residual mass due to the thermally stable ceramic metal oxides. Thus, the utilization of Bauxsol™ as a synergistic additive to existing phosphorus-based intumescent systems appear promising. However, the need remains to investigate the emission products and level of toxicity.

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